

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-241551

(43)Date of publication of application : 16.09.1997

(51)Int.Cl.

C09D 11/00

C09D 11/02

(21)Application number : 08-054559

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(22)Date of filing : 12.03.1996

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## (54) FLUORESCENT INK COMPOSITION FOR EJECT PRINTING

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a fluorescent ink composition for eject printing that can give an image excellent in light resistance and high in fluorescent intensity by mixing a fluorescent dye, an aqueous solvent, transparent solid fine particles, a water-soluble dispersant, an antioxidant, and an antifoaming agent.

**SOLUTION:** This fluorescent ink composition for jet printing is obtained by incorporating, as essential components, (A) a fluorescent dye (e.g. 2, 5- diphenyloxazole), (B) an aqueous solvent (e.g. distilled water), (C) transparent solid fine particles having a particle diameter of 1,  $\mu$ m or less (e.g. titanium oxide), (D) a water-soluble dispersant (e.g. polyoxyethylene octyl phenyl ether), (E) a water-soluble antioxidant (e.g. tin chloride), and (F) a water-soluble antifoaming agent (e.g. propylene glycol). Suitably the ranges of the proportions of the components are such that the component A is 0.001 to 10wt.%, the component B is 50wt.% or more, the component C is 2 to 45wt.%, component D is 0.05 to 5wt.%, the component E is 0.05 to 5wt.%, and the component F is 0.05 to 5wt.%. In passing, a water-soluble resin, an antiseptic preservative, etc., may be added further.

## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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**[Claim(s)]**

[Claim 1] A fluorescence ink constituent for jet printing characterized by containing a transparence solid-state particle with a particle size of 1 micrometer or less, and containing a water-soluble dispersant, a water-soluble anti-oxidant, and a water-soluble defoaming agent further in a fluorescence ink constituent for jet printing using an aquosity solvent, including fluorescent dye.

[Claim 2] 0.001 - 10% of the weight of fluorescent dye, 2 - 45% of the weight of a transparence solid-state particle not more than particle-size 1micrometer, 0.05 - 5% of the weight of a water-soluble dispersant, 0.05 - 5% of the weight of a water-soluble antioxidant, 0.05 - 5% of the weight of a water-soluble defoaming agent, a fluorescence ink constituent for jet printing characterized by containing 50% of the weight or more of an aquosity solvent.

**[Detailed Description of the Invention]****[0001]**

[The technical field to which invention belongs] This invention relates to the fluorescence ink constituent for jet printing which can obtain the print of an image with the high fluorescence luminescence especially with sufficient lightfastness about the fluorescence ink constituent for jet printing containing fluorescent dye.

**[0002]**

[Description of the Prior Art] The fluorescence ink constituent for jet printing used for the method of printing on a printing hand-ed front face with an ink jet printer using the ink containing fluorescent dye, and forming images, such as printing which carries out firefly luminescence by the exposure of excitation energy, such as ultraviolet radiation and infrared light, a graphic form, a line, and a bar code, on the printing front face, and such a method is indicated by official reports, such as JP,62-5079,B, JP,62-24024,B, and \*\*\*\*\* No. 500590 [ six to ], and is well-known.

**[0003]**

[Problem(s) to be Solved by the Invention] However, although the fluorescence ink

constituent for jet printing given in these official reports can form the image of high firefly luminescence to a printing hand-ed front face without absorbency In using the base material front face which has the absorbency of paper, cloth, etc. as a printing hand-ed Since the fluorescent dye in an ink constituent will permeate and diffuse to the depths of a printing hand-ed with a solvent if it prints with an ink jet printer It was economically [ operationally or ] difficult to make high concentration of the fluorescent dye in a printing hand-ed front face, and it originated in that and the technical problem that the firefly luminescence reinforcement in a printing hand-ed front face was inadequate occurred. When the printing hand-ed [ absorbent ] front face was especially colored by Japanese ink etc., lack of the firefly luminescence reinforcement in a printing hand-ed front face had the technical problem were remarkable. Moreover, the technical problem that lightfastness was also inadequate occurred.

[0004] This invention aims at solving the technical problem of the fluorescence ink constituent for jet printing of the conventional technology which was described above. Namely, it is able to make high concentration of the fluorescent dye in a printing hand-ed front face, as a lot of [ lightfastness / lightfastness is good and ] fluorescent dye remains on a printing hand-ed front face, and to form an image with high firefly luminescence reinforcement by the exposure of excitation energy. It aims at offering the fluorescence ink constituent for jet printing which can furthermore be printed to stability.

[0005]

[Means for Solving the Problem] A result of having studied many things in order that this invention persons might solve the above-mentioned technical problem, When it prints on a printing hand-ed front face with an ink jet printer using a fluorescence ink constituent for jet printing which made a transparence solid-state particle contain Even if a printing hand-ed front face is a base material front face with the absorbency of paper, cloth, etc. It fixes without these particles permeating the depths of a printing hand-ed on a printing hand-ed front face. Moreover, since it sticks to a front face of these particles at the time of jet printing before jet printing (in namely, inside of an ink constituent before spreading) of fluorescent dye (namely, when an ink constituent is applied to a printing hand-ed front face and permeates the depths of a printing hand-ed) Osmosis to the depths of a printing hand-ed decreases, and, as a result, fluorescent dye concentration of a printing hand-ed front face becomes high. Therefore, a high mark of firefly luminescence reinforcement is formed of an exposure of excitation energy. Dyeing property to a transparence solid-state particle of fluorescent dye becomes good by making a water-soluble dispersant contain furthermore. By obtaining an image with high firefly luminescence reinforcement, and making a water-soluble antioxidant

contain, by obtaining an image which was excellent in lightfastness, and making a water-soluble defoaming agent contain, knowledge that stable jet printing was attained continuously was acquired, and this invention was completed.

[0006] That is, a fluorescence ink constituent for jet printing characterized by for this invention containing a transparency solid-state particle with a particle size of 1 micrometer or less, and containing a water-soluble dispersant, a water-soluble anti-oxidant, and a water-soluble defoaming agent further in a fluorescence ink constituent for jet printing using an aqueous solvent, including fluorescent dye is offered. This invention is explained below at details. A fluorescence ink constituent for jet printing of this invention can use fluorescent dye, a transparency solid-state particle, an aqueous solvent and a water-soluble dispersant as an additive, a water-soluble antioxidant, and a water-soluble defoaming agent as an indispensable component, and can contain water soluble resin and additives other than the other above if needed further.

[0007] Fluorescent dye used by this invention is fluorescent dye which carries out firefly luminescence by various light, such as ultraviolet radiation, infrared light, or the light, can respond in activity eye and can be chosen suitably. For example, what is necessary is just to choose fluorescent dye suitable for it suitably, in carrying out firefly luminescence, when infrared light is irradiated although firefly luminescence is not carried out in the light. As fluorescent dye, specifically C. I. Fluorescent Brightening Agent 14, 24, 30, 32, 52, 54, 69, 79, 84, 85, 86, 87, 90, 104, 112, 113, 114, 119, 121, 134, 135, 152, 166, 167, 168, 169, 191, 192, 201, 204, 214, 216, 217, 218, 223, 226, 229, 234, 236, 239, 240, 242, 257, 260, 271, 290, 310, 311, 312, 313, 314, 315; C.I. Basic Red 1, 1-1; C.I. Basic Violet 10 and 11:1; C. -- I. Basic Yellow 35, 40, and 95; C. -- I. Basic Blue 7 ; P - quaterphenyl ; P 4-OKISA diazole; 3-phenyl-7-terphenyl; -- 2, 5-diphenyloxazole; -- 2-(1-naphthyl)-5-phenyl oxazole; -- 2-phenyl-5-(4-biphenyl)- 1 and 3 -- (1 and 2-2H-naphthyl)-thioria ZORIRU)-coumarin; 3, 7-screw (diethylamino) FENOKISAZONIUMU nitrate; 3, 7-screw (diethylamino) FENOKISAZONIUMU nitrate; DTTCI which is a laser color (CAS No.3071-70-3), HDITCI (CAS No.23178-67-8), IR-125 (CAS No.3599-32-4), IR-132 (CAS No.62669-62-9), IR-140 (CAS No.53655-17-7), H.I.D.C. Iodide, etc. are mentioned as a typical (CAS No.36536-22-8) thing. Although what is distributed to an aqueous solvent at dissolution or stability is desirable as for these fluorescent dye when a point of the storage stability of a fluorescence ink constituent for jet printing is taken into consideration, it is usable by making a hydrophobic thing stick to a transparency solid-state particle beforehand.

[0008] In this invention, a transparency solid-state particle is blended in order to make high fluorescent dye concentration of a printing hand-ed front face and to obtain an

image with high firefly luminescence reinforcement. Namely, although fluorescent dye permeates in the case of an absorbency printing hand-ed and it is easy to diffuse it with an aquosity solvent at the depths of a printing hand-ed in it, if a transparence solid-state particle is blended into a fluorescence ink constituent for jet printing These particles remain without permeating the depths of a printing hand-ed on a front face. It sticks to a front stirrup of a particle's which remained on the printing hand-ed front face jet printing of fluorescent dye at the time of jet printing, and it controls osmosis to the printing hand-ed depths of fluorescent dye, consequently fluorescent dye concentration of a printing hand-ed front face becomes high.

[0009] What will be colored if "transparence" about a transparence solid-state particle used by this invention penetrates light in addition to transparence of perfect semantics, and a thing which has become muddy are also contained. However, a thing which does not make light penetrate is unsuitable to this invention since firefly luminescence reinforcement falls, and in order to soil a printing hand-ed. Particle size of a transparence solid-state particle must be 1 micrometer or less so that nozzle \*\*\*\* of a jet printer may not arise, and when a point it is made to be easy to remain on a front face of a printing hand-ed is also taken into consideration, it is 0.01-0.5 micrometers preferably.

[0010] As these transparence solid-state particle, by minerals system, in order that titanium oxide, an iron oxide, a calcium carbonate, a barium sulfate, etc. may be mentioned as a typical thing and these minerals system particle may improve distributed stability if needed, what performed surface treatment may be used. Moreover, a hollow-like resin particle manufactured from an acrylic-styrene copolymer given in official reports, such as JP,63-254176,A, etc. by nature system of organic; a non-hollow-like resin particle of a publication water-dispersion [ various ] etc. is mentioned to official reports, such as JP,4-337305,A, JP,5-214194,A, JP,6-16895,A, JP,6-136164,A, JP,6-298879,A, JP,6-322221,A, JP,6-322215,A, JP,7-53913,A, and JP,7-53730,A, as a typical thing.

[0011] An aquosity solvent used by this invention is water independent, or is mixture with a little water miscibility organic solvent relatively [ water / a lot of ] relatively, water is distilled water or ion exchange water preferably, and water miscibility organic solvents are methyl alcohol, ethyl alcohol, isopropyl alcohol, dioxane, an acetone, a methyl ethyl ketone, carbitol, dimethyl sulfoxide, etc.

[0012] In this invention, a water-soluble dispersant is blended in order to obtain an image with high firefly luminescence reinforcement in a printing hand-ed front face which makes easy to dye for fluorescent dye and is especially colored a transparence solid-state particle with Japanese ink etc. Although polyoxyethylene octyl phenyl ether,

the Pori (oxyethylene) dipropyl amine, polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan trioleate, a polyoxyethylene lauryl amine, etc. are mentioned as a typical thing as these water solubility dispersant, it is [ that there is especially no limit ] usable, if it is water solubility and is the dispersant which is effective in raising the dyeing property of fluorescent dye to a transparence solid-state particle.

[0013] In this invention, a water-soluble antioxidant raises firefly luminescence reinforcement of ink in which an image was formed, improves lightfastness further, and it blends it in order to enable it to maintain firefly luminescence for a long period of time. As these water solubility anti-oxidant, hydroquinone, methyl hydroquinone, tin chloride, etc. are mentioned as a typical thing. In this invention, a water-soluble defoaming agent is blended in order to make an image which prevents foaming of ink, and makes stable ink regurgitation possible continuously, and does not have a defect form. As these water solubility defoaming agent, an acetylene glycol, propylene glycol, etc. are mentioned as a typical thing.

[0014] A fluorescence ink constituent for jet printing of this invention A component explained above is contained as an indispensable component. About these blending ratio of coal Fluorescent dye preferably 0.001 to 10% of the weight 0.005 - 2 % of the weight, A water-soluble dispersant three to 35% of the weight preferably two to 45% of the weight 0.05 - 5 % of the weight, [ a transparence solid-state particle ] It is preferably suitable that 0.1 - 2 % of the weight and a water-soluble defoaming agent are [ 0.1 - 2 % of the weight and an aquosity solvent ] 50 % of the weight or more preferably 0.05 to 5% of the weight 0.05 to 5% of the weight for a water-soluble antioxidant 0.1 to 2% of the weight.

[0015] A fluorescence ink constituent for jet printing of this invention Furthermore, so that a transparence solid-state particle may adhere to a printing hand-ed front face firmly if needed So that a particle adhering to a nozzle of a jet printer can remove easily Moreover, polyacrylic acid, Polyacrylate, a styrene-maleic-acid copolymer, a styrene sulfonic-acid-maleic-acid copolymer, Polyester, hydroxyethyl cellulose, polyvinyl alcohol, Water soluble resin, such as a malto sill cyclodextrin and a polyethylene glycol, in 1 - 45% of the weight of an amount; lithium nitrate, Additives, such as electric conductivity regulators, such as a nitrous-acid lithium, ammonium sulfite, ammonium formate, ammonium acetate, lithium halide, and thiocyanic acid soda, and antiseptics, can be contained in 0.1 - 5% of the weight of an amount.

[0016] A fluorescence ink constituent for jet printing of this invention needs to have a property which was adapted for printing by ink jet printer. Therefore, as for an ink constituent, it is desirable for viscosity to be the range whose about 0.8 to 1.2 surface tension about 50 to 3000 ohm-cm and specific gravity is about 20-60 dynes/cm for about one to 10 mPa-sec (20 degrees C) and specific resistance.

[0017] A fluorescence ink constituent for jet printing of this invention Mix and stir all components at once, or fluorescent dye, a transparency solid-state particle, a water-soluble dispersant, a water-soluble antioxidant, and some aqueous solvents are mixed and stirred beforehand. Fluorescent dye is made to stick to said particle, and these and a remainder component are mixed and stirred and it can be prepared by filtering and refining with a filter which has about 1 / ten or less pore size of a diameter of a nozzle of an ink jet printer subsequently used.

[0018] As an ink jet printer which can carry out jet printing using a fluorescence ink constituent for jet printing of this invention, various well-known printers can be used from the former, and an electrification control system, ink on demand, a method that makes an ink constituent breathe out by thermal head are specifically held as a typical thing.

[0019]

[Example] An example and the example of a comparison explain this invention below at details.

After mixing fluorescent dye, a transparency solid-state particle, water soluble resin, an additive, and an aqueous solvent to homogeneity by the blending ratio of coal (unit: weight section) shown in one to examples 1-6 and example of comparison 4 table 1, the pore size 5.0micrometer membrane filter filtered and refined, and the ink constituent corresponding to each example and the example of a comparison was prepared. In addition, the dispersion liquid A of the column of a transparency solid-state particle are a water dispersion containing a sulfonic-acid system surfactant of an acrylic-styrene copolymer hollow-like resin particle. It is 0.5 micrometers in (48 % of the weight of NV(s), and mean particle diameter), and Particle B is an acrylic resin system non-hollow-like resin particle (mean particle diameter of 0.2 micrometers), and dispersion liquid D are [ dispersion liquid C are a water dispersion (NV of 20 % of the weight, mean particle diameter of 0.05 micrometers) of the Nylon particle which is the acrylic-acid graft object of N-methoxymethyl-ized nylon, and ] an albumen-chitosan reactant particle water dispersion (NV of 5 % of the weight, mean particle diameter of 0.05 micrometers).

[0020] On the postcard which smeared away non-printed a postcard and a front face in India ink, dot printing of each ink constituent was carried out with the ink jet printer, and firefly luminescence reinforcement was measured using the spectrophotofluorometer about the printing. The result is shown in the lower berth of a table 1. In addition, in examples 1-2 and the example 1 of a comparison, firefly luminescence reinforcement [ in / for the firefly luminescence reinforcement when irradiating 365nm excitation light / the non-printed postcard of the example 1 of a



comparison ] is shown as a relative value at the time of being referred to as 100. Moreover, in examples 3-4 and the example 2 of a comparison, firefly luminescence reinforcement [ in / for the firefly luminescence reinforcement when irradiating 655nm excitation light / the non-printed postcard of the example 2 of a comparison ] is shown as a relative value at the time of being referred to as 100. Moreover, in an example 5 and the example 3 of a comparison, firefly luminescence reinforcement [ in / for the firefly luminescence reinforcement when irradiating 825nm excitation light / the non-printed postcard of the example 3 of a comparison ] is shown as a relative value at the time of being referred to as 100. Moreover, in an example 6 and the example 4 of a comparison, firefly luminescence reinforcement [ in / for the firefly luminescence reinforcement when irradiating 795nm excitation light / the non-printed postcard of the example 4 of a comparison ] is shown as a relative value at the time of being referred to as 100.

[0021] Moreover, in order to investigate the lightfastness of the printing object which carried out dot printing of each ink constituent with the ink jet printer, the printing object was put on the location of a 5cm directly under of 30W fluorescent lamp, and the firefly luminescence reinforcement after carrying out continuous irradiation for 100 hours was measured like the above. The result is shown in the lower berth of a table 1 as a relative value. Moreover, in order to investigate the fizz of ink, 100ml of each ink constituent was put into respectively separate 500ml measuring cylinder, aeration was performed by the air pump of 1000 ml/min for 2 hours, and the upper bed location of the generated bubble was measured immediately after that. The thing of under the 2 double of the upper bed location of ink before examining the result is shown in the lower berth of a table 1, using "O" and a twice [ more than ] as many thing as this as "x."

[0022] Moreover, in order to investigate the antifoam of ink, after putting 80ml of each ink constituent into respectively separate 100ml bottle and repeating a fall 10 times in the vertical direction, time amount until a bubble disappears was measured visually. What carries out defoaming of the result under for 1 minute is shown in the lower berth of a table 1, using the thing more than for "O" and 1 minute as "x." Moreover, in order to investigate the stability of continuation printing, each ink constituent was continuously printed with the ink jet printer of an electrification control system for 500 hours. It is shown in the lower berth of a table 1, using as "x" that "O", the thing which the printing area changed with time and became narrow, or printing what has printed the result to stability became impossible.

[0023]

[A table 1]

表 1

組 成		実 施 例		比 較 例	実 施 例		比 較 例	実 施 例		比 較 例	実 施 例		比 較 例
		1	2	1	3	4	2	5	3	6	4		
蛍 光 染 料	C.I. Basic Red 1-1	0.04	0.04	0.04	0.01	0.01	0.01	0.05	0.05	0.01	0.01		
	C.I. Basic Yellow 40 H.I.D.C. Iodide IR-140 IR-125	0.04	0.04	0.04									
透 明 固 体 微 粒 子	分散液A (NV5%、平均粒径0.5 μm)	30	60		20			60			80		
	粒子B (平均粒径0.2 μm) 分散液C (NV20%、平均粒径0.05 μm) 分散液D (NV5%、平均粒径0.05 μm)												
水溶性樹脂	ポリビニルアルコール ポリアクリル酸塩 ヒドロキシエチルセルロース	5		10	5		10		5				10
水 性 溶 媒	イオン交換水	58	33	85	68	13	85	23	80	8	80	5	5
	エタノール ジメチルスルホキシド	5	5	5	5	5	5	5	5	5	5	5	5
分 散 剤	ポリオキシエチレンオクチルフェニルエーテル ポリオキシエチレンジプロピルアミン ポリオキシエチレンソルビタンモノラウレート	1	1		1			1		1			
酸化防止剤	ハイドロキノン メチルハイドロキノン 塩化スズ	1	1		0.1			1			0.1		
消 泡 剤	アセチレングリコール	0.4	0.2		0.5	0.2		0.2		0.2			
蛍 光 発 光 強 度	銀印刷ハガキ (A)	135	145	100	130	140	100	145	100	135	100	135	100
	銀印刷ハガキ (B)	30	35	5	25	30	3	35	3	20	5	5	5
耐 光 性 試 験 後 の 蛍 光 発 光 強 度	銀印刷ハガキ (A)	22	24	5	19	21	3	24	3	15	5	5	5
	銀印刷ハガキ (B)	120	130	60	110	120	70	120	75	110	65	2	2
発 泡 性 消 泡 性	銀印刷ハガキ (A)	○	○	×	○	○	×	○	×	○	×	×	×
	銀印刷ハガキ (B)	○	○	×	○	○	×	○	×	○	×	×	×
延焼印刷安定性		○	○	×	○	○	×	○	×	○	×	×	×

[0024] In the examples 1-6 which are the fluorescence ink constituents for jet printing of this invention, firefly luminescence reinforcement was high, and the firefly luminescence intensity ratio to the non-printed postcard of a Japanese ink coating postcard was also as high as 15% or more, and lightfastness, antifoam, and continuation printing stability were still better, and it was that to which it is hard to foam so that clearly from the data shown in a table 1. On the other hand, in the examples 1-4 of a comparison which do not contain a transparency solid-state particle, a water-soluble dispersant, a water-soluble antioxidant, and a water-soluble defoaming agent, firefly luminescence reinforcement was all low, and lightfastness, antifoam, and continuation printing stability were still more inadequate, and it was that to which it is easy to foam.

[0025]

[Effect of the Invention] The fluorescent dye concentration in a printing hand-ed front face becomes high, the fluorescence ink constituent for jet printing of this invention can form an image with high firefly luminescence reinforcement, and since fluorescent dye, the transparency solid-state particle, the water-soluble dispersant, the water-soluble antioxidant, and the water-soluble defoaming agent are contained, even if it prints to an absorbency high printing hand-ed, lightfastness, antifoam, and its continuation printing stability are good, and cannot foam to it further easily.